Ultra-violet Transparency of the Lower Atmosphere, and its Relative Poverty in Ozone.

By the Hon. R. J. STRUTT, F.R.S.

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[PLATE 2.]

Many years ago it was suggested by Hartley* that the limit of the solar spectrum towards the ultra-violet was attributable to absorption by atmospheric ozone, which, as he showed, would give rise to a general absorption beginning at about the place where the solar spectrum ends.

In a recent paper by Prof. A. Fowler and myself,† the evidence for this view was very much strengthened. For it was shown that just on the limits of extinction the solar spectrum shows a series of narrow absorption bands which are eventually merged in the general absorption, and these narrow bands are precisely reproduced in the absorption spectrum of ozone. For my own part, I do not feel any doubt that ozone in the atmosphere is the effective cause limiting the solar spectrum.

The work just cited naturally led to an investigation of the absorption by the atmosphere of ultra-violet light from a distant terrestrial source. This research, though more than once suggested, does not seem to have been undertaken before.

Various sources of ultra-violet light were tried in the course of the investigation. Burning magnesium proved inconvenient, because of the rapidly falling intensity of the spectrum in the far ultra-violet. A cadmium spark was used for short distances up to 1200 yards, and has the advantage of showing strong lines right through and even much beyond the region of strongest ozone absorption. This would have been the best source for long-distance experiments also, if facilities for producing a powerful spark and skilled assistance in maintaining it for long hours had been at hand, which they were not. I was compelled to use a source which would work without attention, and a quartz mercury vapour lamp answered this purpose well, though its strongest lines are not of quite such short wave-length as might be desired.

The source of light (spark or mercury lamp) was placed behind a quartz lens of $3\frac{1}{2}$ inches diameter, arranged to focus it on the distant station. Since

* 'J. Chem. Soc.,' vol. 39, p. 111 (1881).

† 'Roy. Soc. Proc.,' A, vol. 93, p. 577 (1917).

the difference of focus for the visual and extreme ultra-violet regions is very marked, a choice must be made between them ; and since the furthest ultra-violet rays are most weakened by atmospheric scattering, the focus was adjusted for them. In the case of the cadmium spark, the line 2313 was chosen.

Adjustment was made during day time. The spark-gap was fixed at the calculated distance from the lens. The image of the distant station, as seen by daylight, was viewed by means of an eyepiece, and brought on to the spark-gap. To do this, it was essential, temporarily, to stop down the lens to a small aperture, as otherwise the focus adjusted for the far ultra-violet was too indistinct for the visual rays. After adjustment, the diaphragm was removed, and everything left undisturbed till night had fallen.

Nearly the same method was used for the mercury lamp. Here, owing to the large size of the source, chromatic aberration is of less importance, and it suffices to focus for the visual rays. The image of the distant station cannot, however, be well examined with the lamp in place, and it was necessary to substitute cross-wires, which were carried on a support like that of the lamp, and which could be brought into the same position relative to the lens by means of stops.

The mercury lamp was set up at Whitelands, near Hatfield Peveril Station, Essex, where it could be supplied by a private electric installation. The longest range obtainable was across the Chelmer Valley to Little Baddow, a distance of almost exactly four miles (6·45 kilom.). Over most of the range the path of the beam was some distance above the ground, and out of the reach of low-lying mists.

A small portable prismatic camera was used for photographing the spectrum. It was provided with a 60° quartz prism, and a quartz lens of 1 inch aperture and 5 inches focal length. A small telescope with cross-wires was fixed at the proper angle on the top of the instrument, to serve as a finder. When the distant light was on the cross-wires, the spectrum was in focus. The plate holder had of course to be sloped, to allow for the chromatic aberration of the lens, and this made it necessary to recover the exact direction of the source for which the instrument had been adjusted originally.

The camera was designed for broadening the spectrum by slow tilting in the course of the exposure, but this was not found advantageous in practice. Broadening in this way means loss of intensity, and is not required for a bright-line spectrum.* The monochromatic images appear as round dots, not lines, but this is no particular disadvantage.

* It is, of course, much more necessary for dark-line stellar spectra.

The camera was taken each night to the place of observation and set up on a portable tripod in the open air. Dew on the prism was sometimes a source of trouble. Extra rapid plates were used, and in order to determine the limits of transmission, it was necessary to expose till the strong lines in the near ultra-violet were lost in the blur of over-exposure.

A spectrum of the cadmium spark taken at 3600 feet (1100 metres) showed no definite indication of ozone, the whole spectrum being transmitted to λ 2313, right through the region, near λ 2536, where ozone absorption is a maximum.

The best of the mercury lamp spectra are reproduced in Plate 2. Referring to that plate, No. I is the spectrum of the lamp at short range, the wave-lengths of some of the chief lines marked. The extreme range ever observed in the solar spectrum is also shown by the arrow.

No. II is a mercury lamp spectrum, taken with two hours' exposure, on a clear night, at a distance of 4 miles (6·45 kilom.). It will be seen that the spectrum extends as far as wave-length 2536.

The length of this spectrum cannot be compared directly with the length of the solar spectrum, taken near the sea-level, for the equivalent thickness of air traversed in that case would be more than 5 miles, and therefore considerably more than the 4 miles range of the experiment.* We can, however, compare it with the photographs of the solar spectrum obtained by Simony on the Peak of Teneriffe† at an altitude of 3700 metres (12,200 feet).

Now, at this altitude, the atmospheric pressure, reckoned by the usual logarithmic formula, would be about 0·644 of its value at the earth's surface. Taking the "height of the homogeneous atmosphere" at 0° C. as 26,200 feet, the equivalent thickness of air at N.T.P., measured in a vertical direction above the mountain, would be 16,900 feet. The observations are stated to have been made in August, when the sun's declination cannot have been less than 9° north. Assuming the observations to have been made near noon, as no doubt they would be, the sun's zenith distance in latitude 28° north would be not more than 19°. For such moderate distances from the zenith, the thickness of air traversed may be taken as inversely proportional to the cosine of the zenith distance. This makes the thickness of air traversed not more than 17,900 feet.

This is decidedly less than the thickness of air through which the mercury spectrum was photographed. Reduced to 0° C., the latter was about 20,100 feet.

* The lie of the ground did not allow me to get a longer range.

† See Cornu, 'Comptes Rendus,' vol. 111, p. 941 (1890).

We have, then, the following results to consider :—

	Thickness of air.	Ultra-violet limit.
	feet.	
Solar spectrum from near sea-level	29,000*	2948
Solar spectrum from Peak of Teneriffe	17,900	2922
Mercury lamp spectrum	20,100	2536

* This figure is a little vague, as the data for calculating zenith distance are not given.

It is evident that the lower air is far more transparent than the upper air to ultra-violet rays, if equal masses are considered.

This conclusion is opposed to that of Cornu.* His method was to observe near sea-level the limit of the solar spectrum for various zenith distances, obtaining in this way an empirical formula connecting the spectrum limit with the equivalent thickness of average air traversed (reduced to N.T.P.). He then went up to a high altitude above sea-level, and found that the increased length of the spectrum for a given altitude of the sun was in accordance with what was to be expected from his formula, on the assumption that the lower air had the same absorbing power as the average. He concluded, therefore, that this latter assumption was justified.

The results now brought forward, however, clearly prove that it was not justified. Cornu's method is not an advantageous one, as great strain is thrown on the accuracy with which small variations in the position of the spectrum limit are determined. This limit is only a moderately definite quantity, and however carefully the photographic and instrumental conditions may be defined and reproduced, the limit will depend to some extent on the amount of atmospheric haze. These considerations may perhaps account for what I think must, in any case, be considered an erroneous conclusion, for an indirect inference that the lower atmosphere will not transmit rays of short wave-length cannot stand against direct experimental proof that it will do so.

I have spoken so far of the long-distance mercury spectrum as not extending beyond wave-length 2536. But there is no evidence, nor is it probable, that this is a limit in the same sense as the observed end of the solar spectrum. It is known that the solar spectrum cannot be appreciably lengthened by multiplying the exposure many times. But the line 2536 was barely visible in a photograph which was given one hour's exposure, whereas it comes out clearly with two hours'. Circumstances prevented me from trying longer exposures, but there would be no inherent difficulty in exposing for 10 hours on a winter night. Moreover, a more powerful lamp

* 'Comptes Rendus,' vol. 90, p. 940 (1880).

might be used. With these and other improvements, the spectrum of the lamp might probably be prolonged to the point where oxygen absorption begins to be important.

According to the observations of Fabry and Buisson,* the line 2536 is more strongly absorbed by ozone than any other in the mercury spectrum. Since this radiation gets through, it is evident that the apparent limit of the photographed spectrum is not conditioned in any way by ozone.

Although the ultra-violet spectrum is transmitted as far as λ 2536, yet if we compare the long distance spectrum No. II with No. III taken at short distance, it will be noticed how rapidly the latter falls off in intensity as the wave-length diminishes. The exposures were adjusted to give about the same intensity in the yellow and green lines in each spectrum.

There is a cause quite distinct from selective absorption by ozone or any other special constituent of the air, which will account, at any rate in part, for an effect of this kind. I mean the scattering of light by "small particles." These particles are of two kinds—the molecules themselves and the larger particles which give rise to atmospheric haze. The action of the former alone would not be enough to explain the observed diminution of intensity. It can be shown from established theory that the coefficient of absorption K, for light of wave-length λ, has the value

$$K = \frac{32\pi^3(\mu-1)^2}{3N\lambda^4},\dagger$$

where μ is the refractive index and N the number of molecules per cubic centimetre under standard conditions.

From this we find, for λ 2536,

$$K = 2{\cdot}95 \times 10^{-6},$$

which gives for the transmission at 6·44 kilom. (4 miles) the fraction 0·15.

A similar calculation carried out for the less refrangible part of the spectrum shows that here the loss by scattering is almost negligible. Judging by the great increase of exposure required to extend the spectrum to λ 2536, it appears that the transmission for this line cannot be nearly so much as 0·15, and therefore that scattering by pure air will not account for the observed absorption.

In the lower air, however, suspended particles, small compared with the wave-length, but large compared with the molecules, produce a more important effect than the latter. The amount of this effect is so variable

* 'Journal de Physique,' March, 1913.

† Lord Rayleigh, 'Phil. Mag.,' vol. 47, p. 375 (1899); see also Schuster's 'Optics,' 2nd ed., p. 326 (1909).

from day to day that only a general notion of its magnitude can be obtained from known data.

The measurements of Abbot and Fowle* on solar radiation for different altitudes of the sun at Washington and at Mount Wilson, show that 1 mile of air measured vertically from sea-level on average clear days transmits 0·745 of the radiation of wave-length 3987. This makes the coefficient of absorption of such radiation $1{\cdot}83 \times 10^{-6}$ cm.$^{-1}$.

Ignoring changes of refractivity, and assuming as a rough approximation that the absorption coefficient varies as λ^{-4}, we get for λ 2536 the coefficient of absorption $1{\cdot}125 \times 10^{-5}$ cm.$^{-1}$, and the transmission of this ray by 6·44 kilom. (4 miles) of air would be only 0·0007.

This value, which can only be considered as giving the roughest idea of the true transmission under the actual weather conditions of my experiment, would perhaps more than account for the observed enfeeblement of the line 2536, even if no ozone were present at all.

Making use of Fabry and Buisson's values (*loc. cit.*) for the absorption of λ 2536 by ozone, we find that this computed reduction of intensity (0·0007), actually due to atmospheric scattering, could be produced by a layer of ozone 0·26 mm. thick. Although it appears from what has been said that the experiments afford no positive evidence of any ozone in the lower atmosphere, yet they do enable us to give a maximum estimate of the ozone content, though one that may be much in excess of the actual value.

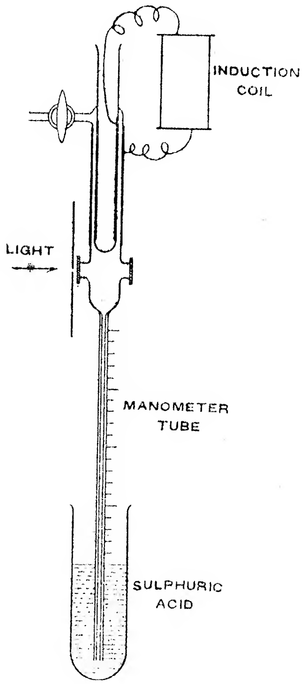
It is impossible to estimate from the present observations how much of the enfeeblement of the ultra-violet spectrum is due to ozone, and how much to scattering. To do this would require very elaborate photometric studies of the transmission of the various wave-lengths, and even so the results would probably not be very secure.†

Let us suppose, however, for a moment that scattering were put out of account. If λ 2536 were enfeebled by ozone only how much ozone could be present? To determine this, spectrum photographs were taken through known thicknesses of the gas. An ozone tube was arranged with quartz windows cemented on with sodium silicate, and a sulphuric acid manometer, as shown (see figure). The quartz windows were 18 mm. apart. The ozoniser was filled with oxygen, allowing the gas to wash through, and to bubble out through the acid below. The pressure was then reduced by

* 'Ann. Astr. Obs. of Smithsonian Institution,' vol. 2, p. 113 (1908).

† In any case, nothing could be attempted in this way without establishing a station from which the distant light could be conveniently observed whenever the weather was suitable, over a long period. I had to be content with a much less ambitious programme, working without assistance during a short summer holiday in the country.

slight suction so that the acid stood at a convenient level in the tube. The discharge was passed for a short time so as to produce ozone, and when the temperature had settled down, the level was read again in order to estimate the contraction.



The volume of the whole apparatus was measured as 12 c.c. Calibration of the narrow tube gave its volume as 32·5 c.mm. per centimetre of length. From these data it may be calculated, taking change of both pressure and volume into account, that 1 cm. rise of sulphuric acid level means 0·890 per cent. by volume of ozone present in the oxygen. Hence, in the distance of 18 mm. between the quartz windows, each centimetre rise of the acid level means a thickness of *pure ozone* (at N.T.P.) equal to 0·152 mm.

A small metal diaphragm was illuminated by the mercury lamp, and the ozone apparatus which has been described was placed in front of it. The spectrum was photographed by the prismatic camera, placed about 15 metres off. The exposure was adjusted so that the yellow and green mercury lines, which are not much affected by ozone absorption, had the same intensity as in the long distance experiments.

Without any ozone the spectrum No. III was obtained. It will be observed that the line 2536 is lost in the blur of over-exposure.

Spectrum No. IV was obtained with a rise of the sulphuric acid equal to 0·7 cm., hence with 0·11 mm. of pure ozone in the absorbing layer. The whole spectrum is still transmitted, but with considerable enfeeblement in the region about 2900.

No. V was obtained with a rise of the sulphuric acid equal to 1·8 cm., hence 0·27 mm. of ozone in the absorbing layer. The line λ 2536 is just visible on the negative, but will probably not come out in the reproduction. It is decidedly less intense than in the long distance spectrum No. II. A slight increase in the ozone beyond this was found to obliterate λ 2536 altogether.

We may conclude then that even if the low intensity of λ 2536 in the long distance spectrum were wholly due to ozone absorption, it would be accounted for by less than 0·27 mm. of ozone in 4 miles of air.

We have already seen that it is quite probable that an effect equivalent to

0·26 mm. ozone is really due to atmospheric scattering. The close agreement of the two figures is, no doubt, largely accidental, but still, allowing for the somewhat uncertain deduction to be made for scattering, it cannot be said that any undoubted effect remains to be attributed to ozone absorption. In any case it is certain that the ozone cannot exceed 0·27 mm.

Now Fabry and Buisson (*loc. cit.*), observing the solar intensity at λ 3000 for various zenith distances, concluded that the observed effects would be explained if the light of the vertical sun passed through the equivalent of 5 mm. of pure ozone, measured at N.T.P. At this rate, for 4 miles of average air at N.T.P., the ozone would be equivalent to 4 mm. of the pure gas, at least 15 times the amount that can be present in 4 miles of air near sea-level. It appears clearly, therefore, from comparison of optical data only, that the air near the ground contains very much less ozone than the average for the whole atmosphere. So far as the optical evidence now available goes, this might be attributed to local impoverishment of the air near ground-level, due for instance to the oxidising action on organic matter; or alternatively it might be due to a stratum rich in ozone, on the outer confines of the atmosphere. A repetition of the mercury lamp experiments at a high altitude on the Alps would help to decide between these alternatives.

The same general conclusion as to the relative poverty in ozone of low-lying air has been drawn previously, on the strength of chemical determinations of ozone, both by Fabry and Buisson (*loc. cit.*), and by Hayhurst and Pring* and also by Pring.† The chemical results of the various experimenters are, however, so hopelessly discrepant with one another that the purely optical method seems to afford a much-needed confirmation. It is wholly free from the main difficulty besetting chemical determinations—I mean the difficulty of distinguishing between ozone and other chemically active substances which may be present in the air, such as hydrogen peroxide and oxides of nitrogen.

Summary.

1. The lower atmosphere is found to be comparatively transparent to ultra-violet light. The line λ 2536 can be detected in the spectrum of a mercury lamp 4 miles distant.

2. The solar spectrum, even when observed from high altitudes when the equivalent thickness of air overhead (reduced to N.T.P.) is less than 4 miles, is limited by atmospheric absorption to λ 2922. Air near the ground-level is, therefore, much more transparent to ultra-violet light than the upper air.

* 'Chem. Soc. Trans.,' vol. 97, p. 868 (1910).

† 'Proc. Roy. Soc.,' A, vol. 90, p. 204 (1914).

3. Since the limitation of the solar spectrum is almost certainly due to ozone, it follows that there must be much more ozone in the upper air than in the lower.

4. Scattering by small particles acts in the same way as ozone to absorb ultra-violet radiation from a distant source, and this action makes quantitative estimation difficult. Even if the observed enfeeblement of λ 2536 were entirely due to ozone, 0·27 mm. of pure ozone in 4 miles of air would suffice to produce it. Taking scattering into account, the quantity is probably much less, and there is no evidence from this investigation that any ozone is present in the lower air.

DESCRIPTION OF PLATE.

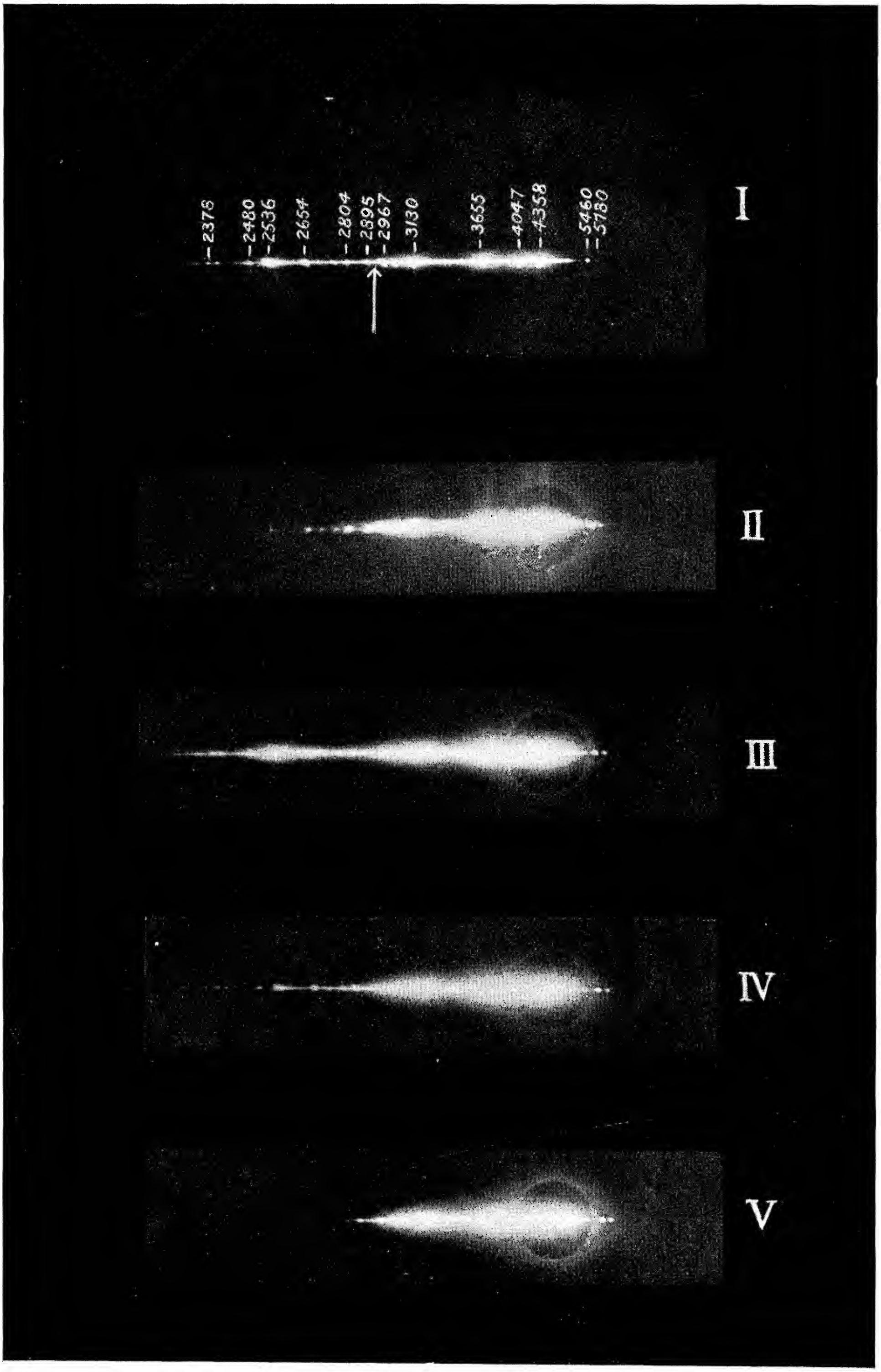
I. Reference spectrum of mercury. The arrow shows the extreme limit observed for the solar spectrum under the most favourable conditions.

II. Spectrum of mercury lamp 4 miles distant. The greater part of the spectrum is unavoidably lost by over-exposure, in order to bring out the ultra-violet end, which extends to λ 2536.

III. Spectrum of the same lamp at short distance. No ozone interposed. This and the remaining spectra are given an exposure bringing the yellow and green lines on the extreme right to the same intensity as the long distance spectrum II.

IV. The same, through 0·11 mm. thickness of ozone. The ultra-violet much enfeebled, though less than in II.

V. The same, through 0·27 mm. thickness of ozone. The ultra-violet feebler than in II showing that the ozone in 4 miles of air amounts to less than 0·27 mm.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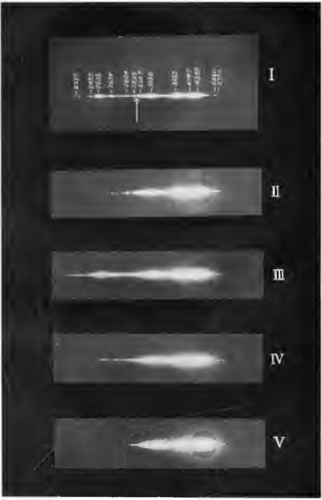

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